REPORT

ARS WORKSHOP

BIOPLASTICS, FILMS AND COATINGS

PEORIA, IL

JUNE 21-22, 1994

F. X. Werber

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FOREWORD

The Idea of a Workshop on Bioplastics, Films and Coatings was formulated in discussions between W. S. Doane and F. X. Werber in late 1993-early 1994. The scope of the subject matter--which product areas to include and exclude--and the format for presentations and discussions were jointly decided.

We owe thanks to Bill Doane for his invaluable contribution and the staff of NCAUR for being great hosts and making this Workshop a success.

This report combines contributions from all the presenters with summary and conclusions for which I will take sole responsibility.

F. X. Werber
July 22, 1994

INTRODUCTION

In part as a result of the increased focus on developing industrial uses for agricultural commodities, over the past 7-8 years a group of programs were started in ARS with similar technological objectives. They all involved the study and development of what in the plastics industries is called "materials of construction", i.e. molded, extruded or solution-cast articles or films with strength, low liquid or vapor permeability and otherwise protective property requirements. All are based on biopolymers, and the properties are very much dependent on molecular weight, physical morphology and chemical properties of the products. The programs at the Regional laboratories (including NCAUR) originated with the mission to broaden the markets for major biopolymers in high value industrial or food uses. (The WRRC project on edible coatings for processed fruit is perhaps an exception. It is aimed at protecting and prolonging the freshness and consumer appeal of cut fruit; however, the product will have to create a new market). The work reported from Winter Haven, on the other hand, is driven by the specific needs of the Florida and California citrus industries.

Because these programs are active in five different locations--the four Regional Research Centers and the Citrus and Subtropical Products Laboratory, in Winter Haven, FL--we thought it important to bring together the participating scientists for a workshop with the overall objective of improving the effectiveness of ARS' total effort in this area. **We specifically restricted attendance at the workshop to ARS scientists and managers, in order to elicit frank exchange of views and suggestions.**

Therefore, the announced purpose of the workshop was: 1) to provide an opportunity to scientists in these programs to gain a minimum understanding of other ARS projects, and the technologies being developed; 2) to generate new collaborations between scientists at different locations; 3) to surface critical gaps in major programs and develop suggestions how these might be filled; 4) to surface possible new program ideas for consideration.

Throughout the workshop, we addressed questions such as the following:

1. How can programs in the various laboratories reinforce each other? Are there obvious areas for interlaboratory collaboration?

2. Are there projects which, though promising, do not have the "critical mass" of effort to reach conclusive results? Are all essential phases of particular projects/objectives being addressed, and if not, how might they be addressed?

3. In regard to Tech Transfer, have the right potential partners been tapped to make effective progress? What can we do to assist forming the right linkages?

The program was structured so as to limit individual presentations to 15 minutes and allow an equal time for discussion and comments. There was a brief (1/2 hour) general discussion period at the end.

HIGHLIGHTS AND CONCLUSIONS

We wanted to capture the maximum amount of information to guide future efforts, both at the individual Regional Research Centers and to aid the National Program Staff in following through for effective coordination. Therefore, we asked individual presenters to furnish abstracts of their presentations (supplied before the meeting) as well as, after the workshop, their individual conclusions which they derived from the discussions. These might include their own thoughts on their future work, and relevant points raised in what turned out to be lively discussion following each presentation. The abstracts and the individual conclusions are incorporated in this report.

INTERLABORATORY COLLABORATIONS

Many of the individual summaries referred to collaborations in general. Following are quotes referring to specific collaborations planned or already initiated:

R. D. Hagenmaier (Winter Haven): "Finally, after hearing of A. Pavlath's plans to apply coatings to peppers and cherries to prevent moisture transfer, I offered him some coatings developed by myself to accomplish that purpose--coatings already used for citrus. Good opportunities for collaboration seem likely."

R. A. Baker (Winter Haven): "The work of Dr. Tom Foglia of ERRC on poly(hydroxyalkanoic) acids, or PHAs, derived from animal fats, may have potential for our uses."

A. E. Pavlath (Albany): "We need to develop better coatings combined with special packaging materials which will match, as much as possible, the carbon dioxide/oxygen transmission ratio of the apple peel in order to limit anerobic respiration. The latter is responsible mostly for changes in flavor and texture. The work at ERRC with pectin-starch combination, the research at Winter Haven using micro emulsion and studies at SRRC with rice protein are especially very promising possibilities for this purpose and cooperative research will be a great help to solve the problem."

M. L. Fishman (Philadelphia): "Finally, Dr. Karel Grohmann is a recognized authority in polysaccharides and citrus by-products. We propose to collaborate with Dr. Grohmann in order to develop new, non-polluting, and cost-effective pectin isolation methods."

F. F. Shih (New Orleans): "We will continue and speed-up our on-going cooperation, combining Leathers' expertise in fermentation and ours in protein and starch modification and characterization, to develop methods for the separation and utilization of the milled rice by-products."

CONCLUSIONS AND SUGGESTIONS FOR MANAGEMENT

Several of the individual summaries/conclusions contained specific suggestions which should be considered:

J. L. Willett (Peoria): "This workshop highlighted the need for increased communication between the various research groups. A procedure of routing technical abstracts of manuscripts to all attendees would be one method; trip report circulation would also be helpful."

Willett also comments: "The tension between research involving high-cost materials such as pectin as opposed to low-cost starch was also evident. I believe it is incumbent upon ARS to continue research involving materials whose benefits and potential may not be immediately obvious today, while also emphasizing the utilization aspects of other, lower-cost materials. Unexpected developments and synergisms will no doubt result from this approach".

M. E. Carr (Peoria): "Therefore, there was, in my opinion, less discussion than desirable on how to solve technology transfer (TT) problems, how to avoid pitfalls, and whether or not future plans of the scientists have merits and/or weaknesses. My suggestion is to more critically emphasize this to those who may participate in any future similar type of workshop."

Suggestions on specific technical directions to be taken are contained in many of the individual Summaries.

ORGANIZERS' CONCLUSIONS

At the outset, I must state my bias, which colors my conclusions. My industrial research and product development background has led me to try to evaluate new developments from the standpoint of ultimate marketability, even at an early stage. This has led me to relate the overall economics of a new development to the anticipated value of the end-product. (It does not mean that one should drop a project if the process economics and the product value do not match up; such a mismatch just means one should look for a higher value end-product or a lower-cost approach).

My conclusions were on several levels:

1. Capability and dedication of the staff.

2. Concentrated effort--do programs have the "critical mass"?

3. Specific suggestions.

I was most impressed with the dedication of the staffs involved in the research at all the locations. The presentations and discussions confirmed not only the competence of the people but the overall spirit and supportive management at the location and the area level.

Starch: NCAUR (Peoria) has been in pursuit of structural materials based on starch for decades, and there can be no doubt that NCAUR has the necessary "critical mass" for this research. This conclusion not only refers to scientists and support staff but also to equipment. On the other hand, Dr. Glenn and his associates at WRRC (Albany) have embarked on a relatively new effort with wheat starch as raw material which I think has much promise. At the same time, this effort, should take advantage wherever possible of the knowledge and technology available at Peoria. "Critical mass" need not be limited to resources--scientists and equipment at one location with proper communication and collaboration, could have "seamless" contact with complementary locations. Therefore, Dr. Glenn's interaction and collaboration with Peoria personnel should be encouraged and supported, e.g. a visit at appropriate intervals (every 3-6 months).

Pectin: Four presentations from ERRC covered the development of films from pectin and blends. The subject of "critical mass" also came up. In my view the progress of this research is admirable, and the scientific effort is probably adequate. The ERRC scientists' ability to characterize biomaterials is probably second to none in the Agency. I am not sure that they are well enough equipped to evaluate films and coatings from an applications standpoint. Their hope is that the Michigan Biotechnical Institute (MBI) will assist materially with commercialization and applications development. Dr. Fishman and his associates should continue to stay alert to bringing in other interested players, perhaps in collaboration also with MBI.

The major gap in the research program on pectin is the cost of pectin. The market prices are in the \$3 to \$4/lb. range (methoxypectin). Dr. Karel Grohmann informs me that hundreds of thousands of tons of orange peel annually are available in Florida, mostly used in animal feed, while some of it is processed, dried and exported to Europe for conversion to pectin. The high cost is due to the concentration of the highly viscous, high-molecular

weight pectin from a 1% acidified solution in ethanol. Karel has pointed out that the understanding of pectin composition is unclear. It is quite possible that other components--proteins, etc.--magnify the complexity in manufacturing. Though the worldwide market for pectin is not insignificant, said to be around 20,000 tons/year, it is unlikely that industry on their own will undertake programs to lower the cost of extracting and producing pectin drastically, without having new markets in view. Therefore, it is incumbent on ARS to take on this responsibility. Dr. Grohmann has agreed to expand his work in this direction this fall, upon the arrival of a scientist transferred to Winter Haven from the Pasadena laboratory.

Finally, I would put forth a general suggestion for management of product development projects in ARS: 1) After the preliminary work necessary to define a new project, it is useful to think of and plan a project in terms of **"milestones"**. In the case of bioplastics or films, the first milestone might be in the definition of properties of a series of materials which have been evaluated (in the course of 2 or more years of exploratory work). The second milestone might be in the broad definition of potential uses of these materials, and the successful search for industry collaborators. The next milestone might be the joint definition and development of an additional product, together with the collaborator. The process of looking ahead and defining these milestones in itself should be useful in planning a multi-year program.

June 21, Tuesday

EDIBLE COATINGS FOR FOODS

8:15- 8:45	R.D. Hagenmaier	CSPL	Fruit Coatings: Problems and Advances
8:45- 9:15	E.A. Baldwin (absent due to illness)	"	Polysaccharide Coatings for Fresh Fruits/Vegetables
9:15- 9:45	R.A. Baker	"	Coatings to Minimize Leakage from Peeled Fruits
9:45-10:15	A.E. Pavlath	WRRC	Edible Coatings Research

10:15-10:30 Break

BIODEGRADABLE FILMS

10:30-11:00	M.L. Fishman	ERRC	Pectin Polyblends for Value-Added Products
11:00-11:30	D. Coffin	ERRC	Physical Properties of Pectin/ Starch Biodegradable Films
11:30-12:00	P.D. Hoagland	ERRC	Films of Pectin/Starch/Chitosan

12:00- 1:00 Lunch

1:00- 1:30	N. Parris	ERRC	Properties of Protein/Poly-saccharide Edible Films
1:30- 2:00	J.W. Lawton	NCAUR	Films from Mixtures of Starch with PVA and EAA
2:00- 3:00	Demonstrations		

NEW PROJECT INITIATIVES

3:00- 3:30	T.A. Foglia	ERRC	Bacterial Conversion of Animal Fats to Biodegradable Elasto-meric Materials
3:30- 4:00	F.F. Shih	SRRC	Edible Films & Coatings from Rice Protein/Starch
4:00- 4:30	J.A. Bietz	NCAUR	Cereal Protein Utilization: Problems and Opportunities
Evening	R.V. Greene	NCAUR	Biodegradation - The Basics (after dinner speech)

June 22, Wednesday

STARCH: PROCESSING AND PROPERTIES

8:00- 8:30	G.M. Glenn	WRRC	Physical and Mechanical Properties of Starch-Based Foams
8:30- 9:00	M.E. Carr	NCAUR	Conversion of Starch by Reactive Extrusion
9:00- 9:30	F.R. Dintzis/ E.B. Bagley	NCAUR	Effect of Processing and Solvent Composition on Measurements of Starch Molecular Size
9:30-10.00	R.L. Shogren	NCAUR	Aging Properties of Extruded Starch

10:00-10:15 Break

10:15-11:15 Demonstrations

STARCH: EXTRUSION PROCESSED BLENDS/COMPOSITES

11:15-11:45	S.H. Imam	NCAUR	Evaluation of Starch-Containing Composites

12:00- 1:00 Lunch

1:00- 1:30	G.F. Fanta	NCAUR	Starch Grafted Thermoplastics
1:30- 2:00	J.L. Willett	NCAUR	Processing of Starch Compounds for Disposables

2:00- ??? Discussion

ABSTRACT

Fruit Coatings. Robert Hagenmaier. Citrus and Subtropical Products Laboratory. 600 Ave. S. NW. Winter Haven. FL 33881.

In examining the relationship between composition and performance of fruit coatings. the speakers biggest difficulty is reinventing coating formulations. Presently used coatings. imperfect as they are. were developed only after decades of technical work to solve some of the problems encountered. This developmental work was. however. almost exclusively proprietary - even most all non-proprietary postharvest work has extensively used coatings of unknown/unreported composition (and therefore compromised its value). The speaker discusses various coating properties. experimental procedures. permitted ingredients. and he offers some ideas for research.

CONCLUSIONS

First, it was a aid to current awareness to listen to M. Fishman, D. Coffin, P. Hoagland, N. Parris and J. Lawton present work on pectin and starch films, which has some relationship to my work on coatings. No new ideas for collaborative efforts were hatched yet, however. Second, appreciated is the advice on availability of electron microscopy at Philadelphia. Finally, after hearing of A. Pavlath's plans to apply coatings to peppers and cherries to prevent moisture transfer, I offered him some coatings developed by myself to accomplish that purpose - coatings already used for citrus. Good opportunities for collaboration seem likely.

Composition and performance of fruit coatings were studied. Use of those comprised mainly of wax make it possible to store citrus fruit with minimal deterioration in flavor and appearance. In contrast, the resin-based coatings commonly used in packinghouses inhibit gas exchange to the extent that off-flavor develops more rapidly, and these impart gloss that is initially higher but shorter-lived. Further development of fruit coatings is dependent on making them less prone to fracture and peeling from the fruit.

ABSTRACT

COATINGS TO MINIMIZE LEAKAGE FROM PEELED CITRUS FRUIT

R. A. Baker and R. D. Hagenmaier

Vacuum infusion of citrus fruit peel with pectinases facilitates its removal, yielding firm whole peeled fruit or intact segments which can be marketed as fresh minimally processed dry-packed products (Baker and Bruemmer, 1989). Enzyme peeled citrus fruit are currently being produced commercially in California, New Jersey, Jamaica, and South Africa. A limitation to the sale of segments or whole peeled fruit in dry-pack format has been their tendency to lose fluids during storage. Excessive fluid loss detracts from the appearance of packaged segments or whole fruit, and results in loss of segment firmness. Efforts to block these deteriorative changes with alginate coatings were only partially successful. The present work was undertaken to find alternative coatings which would effectively block fluid loss.

Edible wax microemulsions were tested for their ability to minimize fluid loss from stored segments and whole peeled fruit. These microemulsions comprised various combinations of edible waxes, fatty acids, and bases in water. Natural waxes such as carnauba and candelilla, and synthetic waxes such as oxidized polyethylene were used in formulations. Fatty acids of varying chain length (C12-C18) were utilized, and either morpholine, NH_4OH or KOH were incorporated as bases.

Fluid loss from uncoated segments varied widely during the season, ranging from 3-8% after one week to 15-45% after four weeks. Microemulsions provided moderate to excellent reduction of this fluid loss. Segments coated with the best emulsions lost only 5% of the fluid lost by uncoated controls after one week storage, and 33% of that of controls after four weeks' storage. Of the fatty acids tested in the coatings, the longer chain acids (palmitic, stearic and oleic) gave more effective formulations than shorter chain acids (myristic and lauric). In general, candelilla and carnauba waxes provided more effective microemulsions than oxidized polyethylene.

Optimum solids levels for coating sections was between 9-12%. Coatings apparently adhered well in storage in saturated atmospheric conditions and in contact with free liquid. These results suggest microemulsions are a viable means to reduce the fluid loss from enzyme peeled fruit packed without liquid cover. Potential effects on flavor and appearance of coated segments are areas requiring future research.

REFERENCES

Baker, R.A. and Bruemmer, J.H. 1989. Quality and stability of enzymically peeled and sectioned citrus fruit. In: *Quality Factors of Fruits and Vegetables*, J.J. Jen (Ed.). American Chemical Society, Washington, DC. p. 140.

CONCLUSIONS

Robert A. Baker
U.S. Citrus and Subtropical Products Laboratory
Winter Haven, FL 33880

The Bioplastics, Films and Coatings Workshop provided everyone working in these areas within the USDA an update on research progress and an excellent chance to interact with each other. As one of the presenters discussing edible coatings, I was reminded that this area of research is being pursued only by our group and by Dr. Pavlath's group. Although the work on starch-based films was most interesting, their physical properties do not lend themselves to application in our problem areas. However, the work of Dr. Tom Foglia of ERRC on poly(hydroxyalkanoic) acids, or PHAs, derived from animal fats, may have potential for our uses. Depending on side chain character, some of these fat derivatives may be able to form coatings with the desired water resistance. Dr. Foglia has not as yet begun production of these materials, but in the future there may be potential for cooperative effort.

ABSTRACT

A. E. Pavlath

EDIBLE COATINGS RESEARCH AT THE WESTERN REGIONAL RESEARCH CENTER

The consumption of fresh fruits and vegetables, generally requires light processing such as the removal of their natural skin and/or cutting them into smaller pieces. Such processing, however, immediately starts changes in properties which may considerably decrease consumer acceptance even after one day. The major properties affecting the consumers' decision are: moisture, color, flavor and texture. Research was carried out at WRRC to develop an edible coating for lightly processed fruits and vegetables to retard these changes during distribution to the consumer. Several coating strategies were taken. These were

- a single application of protein/carbohydrate/lipid layer
- a sequential application of carbohydrate and lipid coatings
- an antibrowning treatment, and
- an antibrowning coating followed by an alginate coatings.

Sliced apples were used in these experiments and the target shelflife was 10-14 days.

The application of a coating as a protein/carbohydrate/lipid emulsion provided protection against moisture losses and discoloration for up to four days while standing in the open air at room temperature. Carbohydrate coatings followed by a lipid layer provided longer protection with increasing relative humidity levels. However, very high humidities occasionally caused mold formation.

The use of calcium ascorbate proved to be essential in preventing discoloration up to 10-14 days. It appears that in addition to the antioxidant property of the ascorbic acid, the presence of the calcium also has a beneficial effect. A taste panel could not differentiate between fresh and calcium ascorbate sprayed apple pieces that were stored at 10°C for three days. While the Whiteness Index did not change noticeably after 10 days, some difference was noted in the texture of the calcium ascorbate treated samples. However, when the calcium ascorbate treatment was followed by the application of analginic acid solution no changes were noticeable in the texture up to 10 days. Further research is being done combining surface treatment with storage in various polymeric containers.

CONCLUSIONS

A. E. Pavlath

EDIBLE COATING RESEARCH: PAST, PRESENT, FUTURE.

The Workshop confirmed that while edible coatings have been applied to whole fruits for a long time, there is only limited information on protecting them once they were cut in any way. Present research on lightly processed products is carried out mostly at ARS laboratories using carbohydrates, fats, proteins and their various combination. Presentations by other ARS scientists working on related projects revealed various possibilities for both cooperation and new directions, and highlighted the crucial need to identify acceptability of coatings (vis-a-vis FDA acceptability) prior to/or in conjunction with the identification of an industrial partner to commercialize coating formulations currently developed. Presently, we can prevent water losses and discoloration in processed apples. We need to develop better coatings combined with special packaging materials which will match, as much as possible, the carbon dioxide/oxygen transmission ratio of the apple peel in order to limit anerobic respiration. The latter is responsible mostly for changes in flavor and texture. The work at ERRC with pectin-starch combination, the research at Winter Haven using micro emulsion and studies at SRRC with rice protein are especially very promising possibilities for this purpose and cooperative research will be a great help to solve the problem.

PECTIN BIOPOLYBLENDS FOR VALUE ADDED PRODUCTS*

Marshall L. Fishman

U.S. Department of Agriculture, Agriculture Research Service
Eastern Regional Research Center
600 E. Mermaid Lane, Philadelphia, PA 19118

ABSTRACT

The objective of this research is to develop industrial products such as edible films from pectin blended with other underutilized polysaccharides. In the 1950's there were attempts to make films for packaging and other uses from low methoxy pectin crosslinked with calcium. The resulting films had poor tear strength. Studies in this laboratory on aqueous solutions of pectin revealed conditions under which pectin was likely to form films either alone or with other biopolymers that were mechanically superior to earlier pectin films. Subsequent studies revealed that pectin could form films with several biopolymers. The most work to date has been done on pectin-starch films. Since certain starches formed better films than others with pectin, we undertook studies on starch in aqueous solution to discover the reason for this finding. Direct interactions with industry and an independent research institute besides literature searches revealed that there were several markets for pectin biopolyblends. Two markets that could be capitalized upon almost immediately are water soluble industrial polymers, and edible films to aid water retention and to form pouches for premeasured food ingredients. Industrial pectin biopolyblend films have an advantage over existing products in that they should be more biodegradable. Edible pectin-starch biopolyblend films should be less expensive to fabricate than existing films of a similar nature made from carrageenan or chemically modified cellulose.

Pectin Polyblends for Value Added Products

Marshall L. Fishman

Conclusions From the Follow-up Discussion:

Dr. Werber appeared to be favorably impressed with the research which was conducted at ERRC concerning pectin/starch films. Also, he appeared to agree that these films had potential to be commercialized because of their unique film forming properties and biodegradability. Dr. Karel Grohmann from CSPL, Winter Haven, FL agreed with our contention that pectin was under-utilized and that this situation was likely to grow worse in that markets for food grade orange and grapefruit pectin have either disappeared or were rapidly disappearing due to superiority of pectin from limes and lemons. He added that the outlook for continued use of pectin as a low value cattle feed product appeared to be dim due to added competition from other countries producing pectin and the greater availability of nutritious by-products from the fuel ethanol industry also now being used for cattle feed. Based upon this assertion, it would appear that the disposal of pectinaceous waste from juice production could pose a serious and costly disposal problem in order for juice producers to comply with laws designed to prevent environmental pollution. Of course producers of apple juice, sunflower oil and beet-sucrose are likely to face the same problem.

Dr. Werber suggested that $1.40/lb was too costly to produce pectin/starch films and not competitive. However, biodegradable PHBV is being commercialized by Zeneca at a projected retail cost of $4.00/lb. The cost to produce it now is about $9.00/lb. ARS is initiating new programs on PHB production despite the fact that the retail costs are not expected to drop much below $4.00 per pound. In order to circumvent the cost concerns, we have identified three target polymers with which pectin/starch films can be priced competitively right now. These are polyvinylalcohol, carrageenan, and hydroxy propylmethyl cellulose which are used today in commercial products.

Dr. Werber also suggested that our group lacked the critical mass required for the further development of pectin/starch films. We anticipated this criticism and have been negotiating a CRADA over the last several months with Michigan Biotechnological Institute (MBI). These negotiations are quite advanced and should be completed shortly. In this agreement, our group shall continue to study basic properties of pectin and starch as needed to support the commercialization of pectin/starch films. MBI has agreed to perform engineering work, background marketing and cost analysis (they have already given us valuable information), and to find venture capitol or a 3rd party company to produce pectin/starch films. MBI and ARS will share equally in any profits from the sale of the technology. I believe that there are several compelling reasons for ARS to enter into the relationship. Ramani Narayen, the principal scientist at MBI with whom I have been working has a proven track record in transferring technology. He is responsible for

developing joint ventures with Cargill (polylactic acid production from corn dextrose), and Japan Corn Starch (production of modified starch plastics). Both of these agreements are based on technology developed by MBI. MBI is not wedded to any particular technology for the production of pectin/starch films. This means that they will consider either extrusion technology or solution casting of films. This is important in that polyvinylalcohol and cellulose films are already being produced by solution technology and this may be the best method of production. An MBI/ARS joint venture is consistent with the mandate of congress to become involved with outside organizations.

Another option to "leverage" our impact on pectin-starch film research is currently being investigated. This is a potential CRADA or other type of alliance with Producers Renewable Products, LLC. This group is committed to building a plant for the economical commercial scale production of sunflower pectin. The presence of such an inexpensive product, capable of producing good films, derived from currently discarded agricultural residues, would be a major boost for our program. We will investigate a partnership, where we can evaluate the functional properties of their pectins and allow them to fine tune their manufacturing procedure to obtain optimum properties in their pectin.

Finally, Dr. Karol Grohmann is a recognized authority in polysaccharides and citrus by-products. We propose to collaborate with Dr. Grohmann in order to develop new, non-polluting, and cost-effective pectin isolation methods.

Several other ARS groups have indicated a desire to collaborate with us based on our demonstrated expertise (publications and presentations) in the characterization of pectin and starch and we have been encouraged to do so. We are eager to collaborate but have two concerns. First, our ability to collaborate has been diminished by the transfer of $75,000 base funds to new ERRC initiatives programs that are of very high priority to ERRC and ARS. Second, any collaboration must not compromise our ability to develop productive CRADA's with outside organizations.

IN SUMMARY:

The Drivers in our research are:

1) Pectin's excellent film forming properties
2) Pectin's ability to form excellent films with starch and other inexpensive polysaccharides.
3) The need for cost-effective, biodegradable replacements for both moderately priced (polyvinyl alcohol, cellulose derivative) and high valued, (carageenan) film made from non-agricultural materials.
4) We need to find new markets for agricultural products (starch).

5) Need to find new markets for pectin-rich fruit processing wastes that are having negative environmental impact and are a financial burden to U.S. industries struggling to compete with non U.S. firms.

The actions items for personnel on 1935-41000-023 are:

1) Develop CRADA with MBI for one purpose only - commercialize a new pectin-based biodegradable film.
2) Develop agreement with Producers Renewable Products, LLC to facilitate the development of inexpensive film-grade pectin.
3) Work with Dr. Karol Grohmann to develop method for inexpensive isolation of citrus pectin.
4) Work with Dr. Thomas Foglia's group at ERRC to develop water resistant pectin/starch PHB laminate films.
5) Continue to develop basic technology and knowledge about pectin-polysaccharide interactions.

Action items for ERRC managers (RL and Center Director):

1) Evaluate Unit resources and consider re-direction of Unit /Center expertise to develop new pectin production techniques.
2) Convert current temporary CWU personnel to permanent status to eliminate critical loss of special skills.

Action items for NPS:

1) Increase "critical mass" in this program area through re-direction, new funding, or other less formal agreements, especially in area of:

   a) film formation,
   b) pectin production methods.

PHYSICAL PROPERTIES OF PECTIN/STARCH BIODEGRADABLE FILMS*

David R. Coffin

U. S. Department of Agriculture, Agriculture Research Service
Eastern Regional Research Center
600 E. Mermaid Lane, Philadelphia, PA 19118

ABSTRACT

The objective of this work is to develop value-added biodegradable plastics from renewable agricultural resources. Blends of high methoxy pectin and high amylose corn starch are showing promise as biodegradable films for use in a variety of applications. Varying compositions of pectin, starch, and plasticizer were cast into self-supporting films from aqueous solution. The dynamic mechanical properties and tensile properties of the films are strongly dependent on the composition of the films. A broad range of useful properties was obtained over a wide variety of film compositions. The rate at which glycerine migrates from the films was also studied.

Summary and Conclusions

The economics of pectin/starch films are favorable compared to other polysaccharide and natural polymers such as carrageenan, hydroxypropylmethylcellulose, and poly(hydroxyalkanoates) which sell for several dollars more per pound. Projected pricing indicates that the raw material costs for the pectin/starch based films will be in the range of $1.40 per pound. Poly(vinyl alcohol), a competitive synthetic biodegradable material sells for $1.48-1.78 per pound. Personnel from CPSC in Winter Haven expressed interest in collaborating on the use of orange and grapefruit peel waste as a source of quality pectin for biodegradable films. Syed Iman from NCAUR expressed interest in collaboration on the extrusion processing of pectin. Both of these areas have the potential to lower the cost of pectin based products and materials.

FILMS OF PECTIN/STARCH/CHITOSAN*

Peter D. Hoagland

U. S. Department fo Agriculture, Agriculture Research Service
Eastern Regional Research Center
600 E. Mermaid Lane, Philadelphia, PA 19118

ABSTRACT

Under somewhat restricted conditions chitosan solutions can be applied to pectin films to give clear bilayer films with good mechanical properties similar to those for pectin/starch films. Low pH retards growth of fungi that were observed when pectin/glycerol films were substrates. The bilayer films gave low permeability to water vapor. Chitosan could be applied to pectin/starch films to reduce water vapor permeability. Biodegradability of pectin/starch films might be altered by chitosan through its nitrogen content. Novel applications of pectin/chitosan films could include incorporating at the interface useful microorganisms that could be triggered to grow upon contact with water. Pectin/starch/chitosan films, fortified with potassium and phosphorous, might also be useful for encasing plant seeds in strips that could be easily planted by the consumer. Bilayer films that incorporate composting microorganisms might be used for mulching leaves.

CONCLUSIONS

Thank you for holding the workshop. I benefited a good deal from participation. I appreciate the contacts I made with other ARS researchers in the biofilm area. I particularly value the specific feedback I received from my presentation. I talked too much about fungal growth and not enough about the main result of our work — namely the successful lamination of biofilms (chitosan and pectin). . All of us here now know that biofilms from natural, renewable sources are possible. We share your concern with the present cost for pectin (and chitosan) and I think some effort should be made to reduce processing costs. With regard to reducing processing costs for pectin, perhaps the technology developed for removing alcohol from beer might be useful. Also, the recently developed extraction of pectin from plant cell walls with imidazole probably has not yet been considered for commercial processing. Could imidazole be recovered and recycled in order to avoid the environmental problems with HCl? We also have some experience in applying ultrafiltration to concentration of pectin in solution. Ultrafiltration might be used to reduce the quantities of alcohol required for precipitation of pectin. We now know enough basic chemistry of pectin (i.e., aggregation, disaggregation) to ask meaningful questions about pectin processing. My strong background in the determination of physical properties of pectin in solution could be useful to quantifying improvements in processing pectin from underutilized orange pulp from the citrus industry. We know how to monitor viscoelestic properties, as well as aggregation.

From my reading of the literature on new applications of biodegradable biomaterials most of the successes are with niche applications. Of course, in those niche applications that involve high value-added products, the cost of biofilms may not be as great a factor as in the case for applications that involve huge amounts of biomaterial. In the future, a combination of political will, hopefully springing from concerned citizens, and diminishing reserves of petroleum will produce an even more favorable climate for biofilms and bioplastics. My impression from the intense discussion about the role of ARS scientists in this area is that part of our mission in the ARS is to do the science necessary to be able to apply biofilm and bioplastic technologies now and in the near future. Good films can be made from pectin and other polysaccharides and our group, under the very capable leadership of Dr. Marshall Fishman, has done and is doing the science necessary for the emerging technology. For those national leaders, who ask for films that are biodegradable and made from renewable agricultural sources, we have positive responses.

One interesting property of pectin/chitosan laminates is that the chitosan surface should be compatible with human skin. A chitosan layer on a biofilm pouch containing hazardous substances would be safe to handle with unprotected hands. The major applications of chitosan laminated to pectin films is to reduce water vapor permeation and to reduce water solubility of the films. For specific applications of pectin/starch films we now have another tool to customize water solubility, water vapor permeation, and bio-compatibility. Compostable bags made from such biofilms would have desirable nitrogen content to enhance composting and would stand up better to wet leaves or damp grass clippings.

I would like to follow up your idea of including a thin layer of oriented mica particles to further reduce water vapor permeation. I would appreciate getting any information you might have on the source or a contact person for this mica preparation. We also want to look at laminates of pectin or pectin/starch with PHVB in cooperation with Dr. Tom Foglia.

With our biofilms made from polysaccharides we have had to focus on hydrophilic properties and water activity. This focus contrasts sharply with the hydrophobic focus on petroleum based films. Because of this refocusing and the basic heterogeneity of polysaccharides, compared to industrial polymers, new science is needed for biofilm technologies. Fortunately, the science of polysaccharides is now at the early stages for application to film technology. Before actually making biofilms in 1993, I was heavily involved in quantification of heterogeneity of gums, pectin and starch and their aggregates with component analysis of high performance size exclusion chromatograms. It is my judgment that our two converging paths, polysaccharide solution behavior and film formation, are now rather well balanced in our program. And, as you pointed out in the workshop, this is the time to assess the state of the critical mass necessary to push the biofilm project forward.

ABSTRACT

FACTORS AFFECTING THE PHYSICAL PROPERTIES OF HYDROCOLLOID/MILK-PROTEIN FILMS AND COATINGS*

Nicholas Parris, D. Coffin, R. Joubran, and H. Pessen

Considerable research has been reported on the use of blends of milk proteins, hydrocolloids, and plasticizers to produce protective films and coatings. Films prepared from polysaccharides and hydrocolloids, eg. pectin, alginate, carrageenan, starch and cellulose form strong films but because of their hydrophilic nature exhibit poor water vapor barrier properties. Films prepared from dried soluble protein e.g. gelatin casein, serum albumin, and egg albumin also exhibit poor water vapor barrier properties, however crosslinking these proteins with lactic acid, tannic acid, or ionized calcium has been shown to increase resistance to water vapor and gas transport. The objective of this research was to reduce hydrocolloid film water vapor permeability (WVP) values through the incorporation of inexpensive milk protein and the proper choice of plasticizer without significantly compromising the film's tensile properties.

Films were cast from blends containing various combinations of (1) whey protein, casein, nonfat dry milk (NDM), or simulated whole milk (NDM + 3.5 wt% butter fat); (2) low or high methoxylated pectin, or algin; (3) sodium lactate, glycerine, or sorbitol. Film blends were qualitatively screened for brittleness, tackiness, strength, haziness, off-color, and graininess. Quantitative parameters were obtained from stress-strain measurements and included tensile strength (TS), modulus, and elongation to break (ETB). Water vapor permeability (WVP) values were determined using a modification of the ASTM E96-80 "Water Method".

Results indicated that alginate films were generally clearer and smoother than films prepared using either of the two pectin hydrocolloids. Sodium lactate was found to be an effective plasticizer and alginate films containing 50 wt% or more sodium lactate had elongations in excess of 13%. Films prepared with sorbitol as the plasticizer had the best WVP values but tended to be stiff and in some cases too brittle for tensile measurements. Addition of SWM to the film blends effectively reduced WVP values by up to 35% with no significant loss in tensile properties.

CONCLUSIONS

From my perspective, I feel that proteins can still offer unique properties to films and coatings but for economic reasons need to be blended with less expensive compounds such as pectin or starch. A number of times diffusion of active ingredients encapsulated in starch particles was mentioned at the Workshop but discussion did not follow on controlling diffusion. In my opinion, three areas of research warrant further investigation:

1. improved methods for isolating proteins and starchs from grain
2. more detailed study of protein-polysaccharide interactions
3. factors affecting the controlled release of active ingredients from encapsulated particles

It may not be necessary to isolate starch free from protein; small amounts of protein can potentially be covalently bound to the starch thus adding to the strength of the product. In addition, proteins have unique properties which can be exploited in the controlled release of compounds from starch (eg. adjusting pH, ionic strength etc.) which do not simply rely on the pore size of the starch particle.

ABSTRACT

Flims from Mixtures of Starch with Poly(vinyl alcohol) and Poly(ethylene-co-acrylic acid)

John W. Lawton
Plant Polymer Research
National Center for Agricultural Utilization Research
Peoria, Illinois

Equations were obtained from response surface models to show how ultimate tensile strength (UTS) and percent elongation at break (%E) of solution-cast films varies with relative amounts of starch, poly(vinyl alcohol) (PVA), poly(ethylene-co-acrylic acid) (EAA) and glycerol in the formulation. Equations found from the response surface methodology were used to optimize the relative amounts of the four components with respect to the physical properties of cast films. The model showed that only glycerol content was important to predict UTS of the films. The model for %E, was more complicated, since there was a three-way interaction between EAA, PVA and glycerol. This model also contained two other terms: a two-way interaction evolving glycerol and EAA, and a $(PVA)^3$ term. In general, %E increased as EAA, PVA and glycerol were increased together. However, increased amounts of EAA could decrease %E if EAA was the only component increased. It is believed that EAA forms complexes with both starch and PVA, thereby increasing compatibility of the two polyhydroxy polymers. As %E increases, UTS of the films decreases. All the films produced in this paper were made with starch contents above 50% to insure an optimum film formulation with at least 50% starch. A mixture of 55.6% starch, 2.8% EAA, 28.3% PVA and 13.3% glycerol is believed to be close to the optimum formulation to obtain films having at least 100%E and UTS of 25 MPA, while still maintaining starch concentrations above 50%.

CONCLUSIONS

Very good films can be made with Poly (ethylene-co- acrylic acid) (EAA), Poly(vinyl alcohol) (PVA), glycerol, and normal cornstarch. Films containing the following ingredients: 40.2% starch, 41.4% PVA, 15.3% glycerol, and 3.1% EAA performed the best. Films were made which had an initial elongation (%E) of over 325%, and still had over 150 %E after 28 days at room temperature and 50% relative humidity (RH). The tensile strength (TS) of the films were about 27 MPa after 7 and 28 days. Films made by replacing normal cornstarch with high amylose cornstarch had a TS of about 27 MPa but had lower elongation of 200 and 100% after 7 and 28 days respectively. All of the films perform very well at 50% RH, but their physical properties change greatly with changes in RH. The film's %E decreases and TS increases with a decrease in RH, and the film's %E increases and TS decreases with an increase in RH. The films become hard and brittle at low RH and soft and rubbery at high RH. Suggestions at the work shop advised the addition of aldehydes to cross link the starch or dichromate to cross link the PVA to make the films more resistant to water. However, these additions would most likely make the films more resistant to biodegradation. A better approach would be to coat the films with a water resistant but biodegradable coating. It would also be of interest to replace some or all of the PVA in the films with pectin, since pectin was reported to have properties similar to PVA.

ABSTRACT

T. A. Foglia

Bacterial Conversion of Animal Fats to Biodegradable Elastomeric Materials

The United States is a major producer of tallow, both edible and inedible. Supply, however, exceeds domestic demand and both the edible and industrial uses of tallow remain either stagnant or in continuous decline. What are needed to overcome this erosion in traditional tallow markets are new ways to use animal fats. One approach to this problem is the microbial bioconversion of animal fats into biopolymers [poly(hydroxyalkanoic acids), PHAs]. PHAs are produced as storage granules or inclusion bodies by a wide variety of bacteria under conditions of metabolic stress in the presence of excess carbon. Normally, the PHAs produced are a family of aliphatic polyesters with alkyl side chains at the β-position. The alkyl substituent can vary from methyl up to dodecyl, depending upon the bacterium and growth conditions used. In general, the bacteria that produce PHAs can be divided into two types: 1) those that produce PHAs with methyl (PHB) and ethyl (PHV) side chains and 2) those where the alkyl group is propyl and larger. The latter PHAs in fact embrace a series of copolymers that possess properties differing from the former polymers in ways that make them especially attractive for commercial exploitation. Because the range of available PHA structures is very wide, their properties may range from elastomers to fibers to films, and hence have attracted considerable industrial interest. The objective of our research is to extend the application potential of PHAs by improving the efficiency of PHA production and increasing the range of polymers that can be produced. To this end, bacteria known to produce PHAs will be grown on tallow as an alternative to currently used feed stocks for the production of PHAs.

CONCLUSIONS

First, I want to inform you that I was greatly impressed with both the quality and diversity of the presentations describing the biopolymer research currently being conducted within the ARS laboratories. From a learning standpoint this conference made me aware of the multiple problems associated with transferring laboratory data to a marketable concept or product. From the problems addressed at this meeting I have a better understanding of the formidable obstacles, besides economics, that must be overcome before a given technology is adopted by industry.

As to my own presentation on "Bacterial Conversion of Agricultural Oils to Biodegradable Elastomeric Polymers" there was only limited discussion by the participants. Most of the relevant points that needed to be addressed on the potential of this area of research were between you and myself in private conversation. From these I believe I have an understanding of the major concerns that you and John Cherry, Center Director for ERRC have expressed. We will attempt to address these as the research unfolds and attempt to exploit this technology to define the more promising aspects of the program and identify milestones for completion of the research. As I told you, I am actively recruiting to fill the vacancies we have for this program. We have two prospective candidates for these positions whose background and training closely match our needs. If successful in hiring them the learning curve for implementing this bioconversion program at ERRC should be shortened considerably. I had private discussions with Bob Shogron, NCAUR, who is the responsible individual for the collaborative research between NCAUR and Zeneca, Inc. on starch-Biopol blends. Our research will be directed to elastomeric materials, from our conversations it was thought that these materials may also be useful in blends with other natural polymers such as starch

Overall, I learned a great deal about the biopolymer programs within ARS and look forward to our entry into this field. I know the challenges are large but I believe they are surmountable.

Development of Edible Films and Coatings from Rice Protein and/or Starch

Fred F. Shih
Southern Regional Research Center

The objective of our research is to promote the use of rice. Specifically, we want to use by-products, such as broken rice kernels and rice bran, from the milling of rice and to convert them into value-added food products in the form of films and coatings.

Broken kernels comprise about 15% of the rice milled in the U.S. and the annual yield of bran is about 1.4 billion lbs. Broken rice consists of starch and protein, and rice bran consists of protein, oil, and fiber. However, there are problems in using these by-products and their components. Rice bran requires treatment such as heat for stablization because of the presence of oil. Rice proteins are difficult to purify and have poor functional properties such as solubility in water. As a result, even though rice bran and broken rice are good sources for protein and starch, they are very much under-used and have limited commercial value. Raw, full-fat bran sells for about $65/ton as animal feed; no established market exists for defatted rice bran. Broken kernels are sold at 6-7 cents/lb, less than half the price of whole rice, mostly to the brewery.

Our mission is to increase the market value for these rice by-products. To do that, we must develop better and more effective methods for their stablization, separation, modification, and utilization. We are currently screening microorganisms and enzymes for treatments that could enhance the separation of rice protein from the starch component and conversion of the starch to useful microbial polysaccharides. Two polysaccharides, pullulan and algin, are of particular interest to us, because they have good film-forming properties.

Generally, protein and starch films are brittle and lacking in strength. Better quality films can be obtained by chemical and/or physical modifications. For instance, phosphorylation has been found to improve film-forming properties for both protein and starch. Recently, we have investigated the effect of protein-polysaccharide interaction on film-forming and other functional properties of the products.

When protein, such as soy isolate and rice protein, was mixed with sodium alginate, the two polymers interacted to form electrostatic complexes. They also formed varying degrees of covalent bonding, depending on reaction time and the presence or absence of the reducing agent sodium cyanoborohydride. On the other hand, protein and propylene glycol alginate (PGA) formed mostly covalent complexes at alkaline pH. The alkylated complexes showed improved film-forming properties. Protein-PGA

films were found to be more readily formed and had greater stability in water than the protein-alginate films.

Pullulan formed transparent and soluble films. The addition of plasticisers such as glycerol, sorbitol, and carbowax made them less brittle, and easier to handle. However, both film strength and its water vapor resistance decreased with increased plasticiser. Best results were obtained for pullulan films with 10% glycerol and 5% carbowax. The cast films remained transparent, easily recovered from the glass plate, and had a tensil strength in the range of 4000-5000 psi. Good films were also prepared with half of the pullulan replaced by rice bran protein concentrate. With the addition of 1% PGA and the casting dispersion at alkaline pH, the films were found to improve in strength and ability to resist water vapor.

A bench-top extruder is being acquired to enhance our processing and film-making capacity. Effort is being made to establish standards for film-product evaluation. Modifications will be carried out and methods developed to ensure the production of rice-based films and coatings for use in foods.

CONCLUSIONS

It is a general consensus that by products from the milling of rice, rice bran and broken kernels, have the potential to be converted into value-added food products including edible films and coatings. It may be desirable that the protein and starch be isolated from the bran and brokens for use in these products. Fermentation is considered an effective way to achieve the separation.

After talking with T. Leathers, a microbiologist at NCAUR, E. Champagne and I have a better understanding of how microorganisms could be screened or grown to develop specific features. We will continue and speed-up our on-going cooperation, combining Leathers' expertise in fermentation and ours in protein and starch modification and characterization, to develop methods for the separation and utilization of the milled rice by products.

We are very impressed by the extrusion demonstration at NCAUR, particularly its film-making capacity. Consultations with individuals including M. Carr, S. Imam, J. Willett, and D. Sessa have convinced us that rice by products, intact or isolated, can be most effectively processed by extrusion. In fact, every phase of the operation including the by-products' separation, stabilization, modification, and utilization can either be enhanced or readily carried out in an extruder. Our discussion with M. Carr concerning the potential of using reactive extrusion for rice by product processing was particularly enlightening.

To us, the workshop was more than successful. We are grateful to all our old and new friends offering us future assistance and cooperation. These three days were a satisfying and rewarding experience.

Cereal Protein Utilization: Problems and Opportunities

Jerold A. Bietz
Food Physical Chemistry, NCAUR, Peoria, IL

Cereal proteins have much potential for many industrial applications. Vital wheat gluten, because of its unique properties, is an especially unique and promising material. Gluten is easily isolated by a simple washing procedure. It is viscoelastic because of the viscous characteristics of its component gliadin fraction, and the elasticity of its polymeric glutenin protein components. It forms films, absorbs water, and has adhesive and thermosetting properties. Gluten is also chemically reactive, so its properties and solubility can be readily modified.

Today, however, little gluten or wheat is used for non-traditional uses. This is surprising, since many studies have shown that gluten can be used not only in foods, but for films, coatings, polymers, resins, inks, detergents, cosmetics, hair care products, adhesives, rubber products, milk replacers, and for many other uses. Today, interest in these applications is increasing because of gluten's many advantages. It is environmentally friendly, biodegradable, renewable, abundant, relatively low in cost, and can reduce dependence on imported petrochemicals.

A recent report for the Wheat Utilization Committee of the National Association of Wheat Growers recommends several promising areas needing further research to increase the use of gluten in non-food products. Such studies could enhance gluten's use in films, coatings, adhesives, emulsions, polymers, rubber, and graft polymers. Central to these recommendations, however, is a recognized need for fundamental research to better define the chemical reactivity of gluten, and to define chemical, physical, and enzymatic procedures to modify gluten's properties, thereby providing new markets and uses for wheat. This is as true today as it was in 1959, when Dr. Fred Senti wrote "Continued emphasis on these gluten studies offers the best hope for discovering new high-value outlets so important for the expanded use of wheat by industry."

Today, growers, researchers, processors, and members of the technical trade must work together to bring these opportunities to fruition. At NCAUR, we plan to contribute to this goal by (a) collaborating with gluten producers to explore new uses for gluten and to better define factors that optimize the functionality and value of vital wheat gluten; (b) investigating possibilities for improved fractionation of gluten to its component classes, gliadin and glutenin, which may separately have new and valuable uses; and (c) continuing to investigate fundamental relationships between gluten components and gluten's functional properties, aimed at optimizing its utilization.

Cereal Protein Utilization: Problems and Opportunities

Jerold A. Bietz
Food Physical Chemistry, NCAUR, Peoria, IL

Cereal proteins, as well as starches, have much potential for many industrial applications. Vital wheat gluten, because of its unique properties, is especially promising, though yet not much used; corn, sorghum, and other cereal proteins present additional possibilities. Wheat gluten can be used for films, coatings, polymers, resins, inks, detergents, cosmetics, hair care products, adhesives, rubber products, milk replacers, and in many foods. Many other possibilities also exist, but few seem to be used, as evidenced by the small amount of wheat directed toward non-traditional uses. Interest in these applications is increasing, however, because of the many real and perceived advantages of gluten. Promising areas for future research, aimed at increasing wheat's industrial utilization, include films, coatings, adhesives, emulsions, polymers, rubber, and graft polymers. Successful realization of these applications requires fundamental investigations of gluten's production, chemical reactivity, modification, and hydrolysis, As Dr. Fred Senti wrote in 1959, "Continued emphasis on these gluten studies offers the best hope for discovering new high-value outlets so important for the expanded use of wheat by industry." We have come full-circle. It is now time for growers, researchers, processors, and the technical trade to work together to bring these opportunities to fruition.

Title: Starch-Based Microcellular Foams

Gregory M. Glenn, Cereal Products Utilization Research Unit, Western Regional Research Center, USDA-ARS, 800 Buchanan Street, Albany, CA 94710

Abstract

The present study was initiated to develop alternative methods of preparing microcellular starch-based foams from semi-rigid aqueous gels (aquagels) and to characterize the impact of the processing method on the physical and mechanical properties of the foams. Semi-rigid aquagels were made from 8% solutions of wheat starch, corn starch, and high amylose corn starch. The aquagels were freeze-dried, or dehydrated in ethanol (alcogels) and either dried in air, extracted with liquid CO_2 and dried in CO_2 vapor, or critical point dried (CPD). The wheat and corn starch foams prepared by air-drying alcogels had densities and mechanical properties similar to liquid CO_2 extracted and CPD samples. Foams of high amylose corn starch could only be made from alcogels by liquid CO_2 extraction and CPD. The mean densities of CPD wheat, corn, and high amylose corn starch foams were 0.23, 0.24, and 0.10 $g \cdot cm^{-3}$, respectively. The compressive strength and modulus of elasticity of the foams was positively correlated with density. The wheat and corn starch foams were weaker under tension than compression due probably to the abundant voids and imperfections in the foam matrix that provided sites for cracks to propagate. These foams also had a high range in elastic modulus (21-35 MPa) and low elastic recovery (13%) compared to high amylose corn starch and freeze-dried samples (3-8 MPa and 27-36%). The range in thermal conductivity (0.024-0.043 $W/m \cdot K$) of the starch foams was comparable to commercial insulation materials. The foam matrix was composed of pores (<2 μm) defined by a network of strands in which were embedded remnants of starch granules. The remnants were most abundant in wheat and corn starch samples. Freeze-dried foams had large, nonuniform pores with a continuous cell wall structure that conferred relatively high tensile strength.

Conclusions

Various potential applications of the research presented were discussed at the end of Dr. Glenn's remarks. One application discussed in some detail was that of flavor encapsulation. Aerogels formed into small spheres were made and found to absorb six times their weight in oil. The comment was made that other polymer products exist that absorb similar or even higher amounts of oil. Dr. Glenn explained that the starch product was unique in that it is food grade and that it releases the oil when exposed to moisture. Another application involved compression molding starch aerogels into microwavable food trays which have plastic-like properties. The question was asked about the heat resistance of the trays. The trays have been tested with DSC and found to withstand temperatures of up to 350 °F. The question was asked about the tray melting during microwave cooking. The product would likely need to be coated with a film forming moisture barrier. The work presented by Dr. Lawton provided some possible solutions and could be a potential area of collaboration. The unique properties of starch aerogels summarized from the study are: high compressive strength, high oil absorption, low thermal conductivity, high porosity or surface area. Although starch aerogels may be expensive to process using the more typical methods, Dr. Glenn explored various alternative drying methods that are more cost effective.

ABSTRACT

Conversion of Starch by Reactive Extrusion

Merle E. Carr
Food Physical Chemistry Research
NCAUR, Peoria, IL

The objective of this research is to expand the utilization of corn and wheat for nonfood applications. The approach is to explore the use of a corotating, fully intermeshing, twin-screw extruder as a reactor for converting starch and flours to chemicals and polymeric derivatives and to characterize, analyze, and evaluate these products for new and/or improved uses. Emphasis is placed on the development of new extrusion processing techniques as well as product utilization. In this area of research starch has been converted to glycosides, starch graft copolymers, cationic and anionic starch derivatives, and starch encapsulated pesticides for a variety of potential industrial applications. The glycosides have been shown to be useful as chemical intermediates for preparation of rigid urethane foams with excellent basic properties and also useful in expanded research as the polyether polyols for flexible urethane foams. Starch graft copolymers, prepared from acrylonitrile and acrylamide, have been found useful as absorbents, flocculants, and coating adhesives, while the cationic starches have been studied and found useful for de-emulsification and flocculation of oil in wastewater streams. Pesticides have been encapsulated in starch matrices with the process successfully scaled-up for potential industrial application. Collaborations have been developed with several industries and universities. Future work will involve efforts to bring both product and process development to fruition and to develop new thermoplastic copolymers through reaction of starch with reactive synthetic polymers.

CONCLUSIONS

This memo responds to your request for feedback info from participants of the subject workshop above. In your memo to Doane and others, March 31, 1994, you requested that the presentations should include background, objectives, end uses, industry contacts, obstacles, and future plans. As you may or may not recall, I followed these instructions to the letter. However, most of the others left out much of this type of information, and many discussed only their research results/data. Therefore, there was, in my opinion, less discussion than desirable on how to solve technology transfer (TT) problems, how to avoid pitfalls, and whether or not future plans of the scientists have merits and/or weaknesses. My suggestion is to more critically emphasize this to those who may participate in any future similar type of workshop. This may require, for example, a special and more emphatic memo on these issues to the invited participants. With respect to other aspects of the workshop, it appears we are not "top heavy," nor are we duplicating our research, and that there are some instances where additional inter- and intra-laboratory collaboration could be developed. However, in my opinion, "critical mass" is lacking in many cases, resulting ultimately in lost research. This problem is not new, of course, but always needs special attention at the right time. Regarding TT activities, future workshops could more strongly stress the importance of carefully screening collaborations between the scientists and industry so that ARS is more frequently a true winner. Undoubtedly, your workshop was an overall success and sets the stage for future related workshop seminars.

Intrinsic viscosity and flow properties of processed starches.

Frederick R. Dintzis/Edward B. Bagley
Food Physical Chemistry Research
NCAUR, Peoria, IL

Abstract

The objectives of these investigations are: 1) to determine the relationship between the hydrodynamic volume of starches as altered by thermal processing and 2) to demonstrate that the amylopectin of waxy maize has significantly different flow properties than the amylopectin of dent maize. The attainment of these objectives will provide basic information about the effects of processing upon the molecular structure of starch and will describe previously unreported behavior of waxy maize. In general, the intrinsic viscosity of starches decreased as severity of thermal treatment increased. An unexpected characteristic of thermally treated waxy maize was that the viscosity of 6% dispersions was extremely sensitively to intrinsic viscosity changes in the narrow range of 180 to 165 ml/g. In contrast, viscosity of waxy maize dispersions were relatively insensitive to changes in the lower intrinsic viscosity values (<160 ml/g) caused by more severe treatments. Shear sweep studies showed that waxy miaze solutions in water, dimethyl sulfoxide or 0.2 N KOH exhibited dilatancy. Photomicrographs of the sheared solutions taken with phase contrast optics showed evidence of structure formation. These effects did not occur with solutions of dent maize. We infer from this evidence that the amylopectin of waxy maize is significantly different in behavior from that of normal dent maize.

Participant Summary & Conclusions

Werber Workshop, June 21-22, 1994, Peoria, IL

The most useful aspects of the meeting to me were: 1) The discussions of CRADA experiences and thoughts on how to judge effectiveness of prospective CRADAS, 2) The reinforcement of my belief that a fail-safe path for both researcher and ARS is mandatory so that positive results of efforts are assured, and 3) The overview of the scope of research efforts activities that was generated by the presentations. Given the stated magnitude of pectin sources available, the suggestions to increase and alter efforts to utilize pectins seemed sensible to me.

ABSTRACT

AGING PROPERTIES OF EXTRUDED STARCH

Randal L. Shogren and Brian K. Jasberg, National Center for Agricultural Utilization Research, ARS, USDA, Peoria, IL.

The structural and mechanical properties of extruded high amylose and normal cornstarch were studied as a function of time and humidity in order to determine the suitability of high amylose cornstarch for use in biodegradable plastic materials. After extrusion at 170 °C and 20-30% moisture, high amylose starch was mostly amorphous with small amounts of V and A type crystal structures. Tensile strengths for the extruded high amylose starch ribbons were rather stable with time (65, 50 and 35 MPa at 20, 50, 80% r.h.) and were higher than those for normal cornstarch (25, 40 and 15 MPa after 90 days at 20, 50, 80% r.h.) Elongations at break declined gradually for high amylose starch (6, 11 and 11% after 90 days at 20, 50, 80% r.h.) while rapid declines were seen for normal cornstarch at higher humidities (3, 9 and 3% after 90 days at 20, 50, 80% r.h.)

Differential scanning calorimetry revealed that normal cornstarch aged at high humidity had much larger sub-T_g endotherms than high amylose cornstarch. These endotherms reflect decreses in enthalpy and free volume which occur in amorphous polymers due to structural relaxation. It appears, therefore, that plastic materials prepared from gelatinized or melted high amylose cornstarch should have greater strength and flexibility and slower physical aging than those prepared from gelatinized normal cornstarch.

AGING PROPERTIES OF EXTRUDED STARCH
Conclusions and Need for Further Research

R. L. Shogren

Conclusion:

The embrittlement of extruded normal cornstarch is due to relaxation of amorphous starch to a lower volume and energy state. High amylose cornstarch has slower aging presumably because greater crystallinity and fewer chain ends slow the rate of high amylose starch relaxation.

Need for Further Research:

Loose fill foam packaging peanuts prepared from modified high amylose cornstarch are currently being marketed. These still suffer, however, from problems with brittleness at low humidities and after aging. Studies of the effect of starch chemical modification and novel plasticizer addition may help resolve these problems.

The water sensitivity of starch foams and films greatly limits their acceptability for many applications such as foamed food trays, cups and food packaging films. Coating/laminating starch based materials with biodegradable, water resistant polymers could greatly increase the potential of starch based plastics to replace petroleum based commodity polymers.

ABSTRACT

Evaluation of starch-containing composites. Syed H. Imam. Biopolymer Research Unit, NCAUR, Peoria, Illinois.

Evaluation of biodegradable plastics engineered by incorporating agricultural materials into plastic resins is the main focus of our research. In one approach, blends have been prepared to by adding agricultural materials and residues in starch-containing blown films and molded materials to add value and to achieve a higher degree of biodegradability. At the same time considerable efforts have been made to develop many suitable techniques for evaluating the biodegradation of such starch-based materials when exposed in laboratory cultures or in natural environments. Research efforts of past several years will be reviewed.

CONCLUSIONS

Summary: Bioplastics, Films and Coatings Workshop--Syed H. Imam

Overall, this workshop was very useful for several reasons. Firstly, opportunity was provided to learn about research and development endeavors in this particular area of science at other ARS locations. Particularly, the in-depth and stimulating discussion following every presentation was a valuable learning experience. Secondly, information gained about a variety of research approaches and methodologies, as well as technology transfer efforts were of considerable importance for everyone who attended the workshop. The workshop also allowed participants to develop several contacts for possible future collaboration on mutually interesting research problems. In this spirit, I certainly believe future workshops like this will provide more opportunity to learn and educate each other and to create an atmosphere of cooperation between locations rather than competition.

ABSTRACT

Starch Grafted Thermoplastics

G. F. Fanta
Plant Polymer Research,
National Center for Agricultural Utilization Research
USDA-Agricultural Research Service
Peoria, IL 61604

Polymer composites in which thermoplastic polymers are chemically bonded to starch (graft copolymers) are easily prepared by generating free radical sites on the starch backbone and then allowing these sites to react with vinyl or acrylic monomers. This method has been used to prepare starch-polystyrene and starch-poly(methyl acrylate) graft copolymers containing about equal weights of starch and synthetic polymer. Preparative techniques for these two polymer systems will be reviewed. Extrusion processing yields tough, flexible plastics from poly(methyl acrylate) graft copolymers, whereas plastics obtained from polystyrene graft copolymers are brittle and appear to have limited utility. An important property in extrusion processing of these starch graft copolymers is the absence of die swell as the plastic leaves the extruder die. Die swell does not take place because of the rigid starch matrix, which prevents these polymers from melting. We have evidence that plastic formation takes place through pressure fusion of heat-softened graft copolymer granules in the high-pressure region of the extruder die. Tests performed on starch-g-poly(methyl acrylate) have verified that these plastics support microörganism growth. Starch-poly(methyl acrylate) graft copolymers may also be extrusion-blown into continuous films, provided that starches or starch derivatives in water solution are used for the grafting reaction. An interesting and useful property of these films is their ability to shrink in size when placed in a high-humidity atmosphere at room temperature.

STARCH GRAFTED THERMOPLASTICS
Conclusions and Need for Further Research

G. F. Fanta

There is need for research in the following specific areas:

1) Use of starch-g-PMA in the preparation of loose-fill foam packaging. A small company near Peoria is attempting to commercialize these starch-based foam products and needs our help in optimizing formulations. This same company is exploring other commercial possibilities for starch-g-PMA, for example, flexible tubings, shotgun wads, and components for shoes.

2) Explore the possibility of using the Fe^{+2}/H_2O_2 redox system as an inexpensive alternative to ceric initiation. Ceric ammonium nitrate is expensive and adds an appreciable amount to the cost of production, even in the small amounts needed to initiate polymerization.

3) Look for niche markets for extrusion blown starch-g-PMA shrink films and for companies willing to explore commercial possibilities.

4) Further explore the advantages of using cereal flour in these graft polymerizations as an alternative to starch. For example, it was discovered under a CRADA (with AURI of Minnesota) that in contrast to starch-based polymers, flour-g-PMA could be extrusion blown into thin films without the necessity of dissolving or gelatinizing the flour beforehand. This discovery significantly reduces the cost of production.

5) Explore the co-grafting of other monomers (e.g. butyl acrylate) along with methyl acrylate to see whether the Tg can be lowered sufficiently to make these starch graft copolymers suitable for low temperature applications.

ABSTRACT

Processing of Starch Compounds for Disposables

J. L. Willett, PPL
National Center For Agricultural Utilization Research,
Agricultural Research Service,
U.S. Department of Agriculture,
Peoria, IL 61604

The properties of thermoplastic starch are dependent upon shear and thermal history, and the amount and types of additives. The characterization of the melt rheology of starch compounds is important for establishing processing parameters. The results of studies on extrusion temperature, moisture content, and additive effects are summarized in this presentation. Additives influence the melt rheology according to their ability to form inclusion complexes with the amylose in starch. Their effects can be interpreted in terms analogous to those used in PVC compounding, namely internal vs. external lubrication.

CONCLUSIONS

The workshop was a welcome opportunity to meet other researchers in ARS who are working in the area of materials, and to become familiar with their research. There are clearly areas in which programs at different locations can reinforce each other. Extrusion expertise exists at NCAUR and polysaccharide characterization expertise is at ERRC and SRRC, for example. I believe the best route to cooperation between groups is by the individual scientists. This workshop highlighted the need for increased communication between the various research groups. A procedure of routing technical abstracts of manuscripts to all attendees would be one method; trip report circulation would also be helpful. Discussions with other researchers during the meeting highlighted the importance of extrusion processing. Increased communication is necessary to prevent duplication of work and provide effective use of personnel and equipment in this area; there is no need for each group to reinvent the wheel. The tension between research involving high-cost materials such as pectin as opposed to low-cost starch was also evident. I believe it is incumbent upon ARS to continue research involving materials whose benefits and potential may not be immediately obvious today, while also emphasizing the utilization aspects of other, lower-cost materials. Unexpected developments and synergisms will no doubt result from this approach. In summary, the important lesson of this workshop for me was the need to encourage and enhance communication between various researchers in ARS.

CONCLUSIONS

R. V. Greene

As requested, I submit the following statement regarding my thoughts following the Bioplastics Workshop. (Note that they are centered around packaging materials and omit edible films, which is a field on the periphery of my expertise):

Realization of a viable market for degradable packaging formulations hinges upon the production of quality materials at a price equivalent to that of petroleum derived plastics. Given such a cost constraint, development of formulations from bulk renewable resources, such as starch, cellulose and possibly pectin is an attractive approach. However, to achieve the quality demanded by the North American consumer, it is likely that higher cost fermentation products (PHBV, PLA) will play a role in a successful formulation (blend). Alone these latter materials can be marketed for speciality uses where price is not a concern, such as for medical applications and packaging of a high value item. Alternatively, cost constraints may be circumvented by legislative action.

ATTENDEES LIST

Frank Werber	NPS
Karel Grohmann	CSPL
Robert Hagenmaier	CSPL
Robert Baker	CSPL
Attila Pavlath	WRRC
Dominic Wong	WRRC
George Robertson	WRRC
Gregory Glenn	WRRC
Antoinette Betschart	WRRC
Marshall Fishman	ERRC
David Coffin	ERRC
Nicholas Parris	ERRC
Peter Hoagland	ERRC
Thomas Foglia	ERRC
Kevin Hicks	ERRC
John Cherry	ERRC
Frederick Shih	SRRC
Elaine Champagne	SRRC
Peter Johnsen	NCAUR
William Doane	NCAUR
Julious Willett	NCAUR
George Fanta	NCAUR
Randal Shogren	NCAUR
John Lawton	NCAUR
Robert Wing	NCAUR
Donald Trimnell	NCAUR
Brian Jasberg	NCAUR
Edward Bagley	NCAUR
Frederick Dintzis	NCAUR
Merle Carr	NCAUR
Jerry Bietz	NCAUR
Leo Cunningham	NCAUR
Floyd Huebner	NCAUR
Joseph Lazlo	NCAUR
Jacob Lehrfeld	NCAUR
Richard Greene	NCAUR
Syed Imam	NCAUR
Tim Leathers	NCAUR
Jeff Ahlgren	NCAUR
John Rothfus	NCAUR
Walter Wolf	NCAUR